

## Internal Molecular Motions in Crystals. The Estimation of Force Constants, Frequencies and Barriers from Diffraction Data. A Feasibility Study

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### Abstract

In this paper the possibility of obtaining information about internal molecular motions in crystals from the atomic vibration tensors supplied by X-ray or neutron diffraction studies is examined. From published or deposited tables of vibration tensor components, torsional amplitudes and corresponding quadratic force constants for about 300 librating groups in more than 125 crystal structures have been estimated. The groups include methyl, trifluoromethyl, trichloromethyl, *tert*-butyl, nitro, carboxy, amino, ammonio, and methylene. Energy barriers have been estimated for the torsional motions on the assumption that these are governed by simple sinusoidal potential functions. Some of the derived values are in reasonable agreement with those obtained by other methods; others show disagreements, which may indicate the influence of the crystal environment. The scope and limitations of the method are discussed in some detail. It seems to be a valuable complement to other methods of studying torsional and similar relatively 'soft' intramolecular motions; in particular, it can provide unambiguous resolution of different internal motions in a given molecule. The method should also be useful as a probe of intermolecular potential functions.

### Introduction

Although anisotropic atomic 'thermal parameters' from crystal structure analyses have been used in a limited way for more than a decade for the estimation of torsional frequencies and barriers for internal molecular motions the method is not widely known, even to specialists in the study of torsional motions in molecules. For example, it is not mentioned in two recent books reviewing large-amplitude intramolecular motions (Orville-Thomas, 1974; Lister, MacDonald & Owen, 1978), although numerous other experimental

techniques for studying such motions are described, some in considerable detail.

Our purpose in the present work was to test the feasibility of using conventional anisotropic Gaussian atomic vibration parameters from X-ray as well as neutron diffraction analyses for the estimation of force constants, frequencies, and energy barriers to internal molecular motions (chiefly torsional) in various classes of compounds. There is nothing novel in our approach, but such a survey could not have been made a decade ago; there were then too few crystal structure analyses of the required accuracy.

### Background

Cruickshank (1956*a*) first showed how anisotropic Gaussian vibration parameters could be used for estimating rigid-body librational and translational motion of molecules in crystals, and he also indicated how the first rather imprecise results for naphthalene could be related to spectroscopic and thermodynamic properties of the crystalline compound (Cruickshank, 1956*b,c*). The concepts behind Cruickshank's approach were later sharpened and extended by Schomaker & Trueblood (1968), who showed how it should be modified to deal with noncentrosymmetric molecular site symmetries as well as centrosymmetric ones. Over the years the rigid-body model has been applied to derive information about vibrational motion in countless molecular crystals [see, for example, Willis & Pryor (1975); Dunitz (1979)].

Studies of intramolecular motion in crystals were pioneered by Johnson (1970), with his segmented-body approach, and by Hamilton and his collaborators in their neutron-diffraction studies of amino acids and other molecules containing methyl groups (Hamilton, Edmonds, Tippe & Rush, 1969; Schlemper, Hamilton & La Placa, 1971; Lehmann, Koetzle & Hamilton, 1972), although torsional amplitudes and frequencies had occasionally been estimated even a decade earlier (e.g. Trueblood, Goldish & Donohue, 1961). Many papers of the Hamilton group include estimates not

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only of amplitudes of  $-\text{CH}_3$  and  $-\text{NH}_3^+$  libration, but of the corresponding force constants, frequencies and torsional potential barriers as well. However, comparatively few others (*e.g.* Prince, Schroeder & Rush, 1973; Prince, Dickens & Rush, 1974) have followed Hamilton's lead, and studies of torsional modes, beyond the estimation of amplitudes, have been limited mainly to structures determined by neutron diffraction. A simple one-parameter model for estimating a torsional libration amplitude about a defined axis (Dunitz & White, 1973) has been applied successfully to neutron and X-ray vibration parameters for a variety of librating groups (Trueblood, 1978). Recent success in estimating plausible magnitudes of torsional barriers from precise X-ray structure analyses (Seiler & Dunitz, 1980; Kai, Knochel, Kwiatkowski, Dunitz, Oth & Seebach, 1982) led us to feel that as the number of highly precise and accurate X-ray structure determinations continues to increase at a growing rate, this approach could serve as a useful complement to other experimental methods as well as to theoretical ones for estimating dynamic parameters associated with intramolecular motions.

The other experimental methods are based mainly on various spectroscopic techniques – high- and low-resolution microwave, Raman, far-infrared, NMR, neutron inelastic scattering – together with gas-phase electron diffraction, and all of them have significant limitations.\* None can provide the resolution of different internal motions in a complicated molecule that can sometimes be achieved from analysis of individual atomic vibration tensors derived from single-crystal diffraction data.

### Procedure

We had already established that the one-parameter Dunitz & White (1973) model for torsional libration gave results not significantly different from those of more elaborate models, even for r.m.s. amplitudes as high as 0.4 rad (Trueblood, 1978). For the present study we have continued to use this model in an updated version of the computer program developed earlier. Most of the data were taken from the literature, although a few are from our own published and unpublished work. We made extensive use of the Cambridge Crystallographic Database (CCD) files

\* A detailed recapitulation of these limitations seems superfluous in this context. We merely point out that some of these experimental methods are limited to the gas phase, while in others even the interpretation of the primary measurements (*e.g.* frequencies or rates) can be highly uncertain [see *e.g.* the discussion of methyl torsional frequencies by Lambert, Nienhuis & Finzel (1981) (NMR method) and by Rush (1967) (neutron inelastic scattering method) or the difficulties in far-infrared measurements alluded to by Durig and his collaborators in their papers cited in the bibliography to Table 1].

(Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) for locating structures of interest. For many such structures the atomic vibration tensors have not been printed in the primary publication but deposited instead. This has not made our work easier, but we are pleased to acknowledge the efficient service of the Executive Secretary of the IUCr in providing deposited material promptly and free of charge. We have concentrated mainly on librational motions of a few fairly representative chemical groupings. We made no effort to examine every reported structure containing a particular group, but limited ourselves rather to examining enough examples to show a pattern or suggest the beginnings of one. In all, we made calculations for around 300 librating groups in more than 125 structures. The results for more than 230 groups are reported or summarized in Table 1 and Figs. 2 to 5.

Bibliographic data for the structures examined in our study are given in the Appendix, with an accompanying serial number that is used for reference in the figures and in Table 1. For structures included in the CCD file before May 1982, the REFCODE and the chemical name of the compound are also given. These structures are listed in alphabetical order of the REFCODE and are followed by the remaining structures in alphabetical order of the name of the compound (sometimes a trivial name).

When there were many structures containing the group of interest to choose from, we selected on the basis of the ease of obtaining the vibrational parameters, the reported precision of these quantities, and the general interest and significance of the possible results (*e.g.* the presence of several groups, some of which might be chemically but not crystallographically equivalent). X-ray structures containing atoms of atomic number higher than 17 (Cl) were rejected, although with data of the highest quality it is possible to obtain meaningful vibration parameters for C atoms even in the presence of an atom as heavy as Ru (Seiler & Dunitz, 1980). Some structures contained two crystallographically independent molecules in the asymmetric unit; these are designated by the letters *A* and *B* following the reference number of the structure in Figs. 3 and 5. This situation in principle permits distinguishing intramolecular from intermolecular effects, but we have not attempted to carry this through in any detail in the present survey.

Although even rather imprecise vibration parameters can sometimes reveal quite clearly torsional motions of sufficiently high amplitude (a few of the results cited below are based on demonstrably poor parameters, some even derived from visually estimated film data!), we selected primarily vibration parameters derived within the last decade from diffractometer data of relatively high precision. We routinely applied

Hirshfeld's (1976) 'rigid-bond' test and its generalization (Rosenfeld, Trueblood & Dunitz, 1978) in assessing the quality of the atomic vibration parameters. The former test is based on the postulate that if  $z_{A,B}^2$  is the mean-square vibrational amplitude of atom  $A$  in the direction of atom  $B$ , then  $\Delta_{AB} = z_{A,B}^2 - z_{B,A}^2 \sim 0$  for any pair of bonded atoms of roughly comparable mass. In a rigid molecule, by definition  $\Delta_{AB} = 0$  for every pair of atoms so the value of  $\langle \Delta_{A,B}^2 \rangle$  should be approximately the same when averaged over nonbonded pairs as over bonded pairs. Hence these tests not only give an idea of the quality of the data, but also serve as a useful diagnostic of the presence of internal molecular motions. Some structural studies that seemed *a priori* likely candidates for inclusion had to be rejected because the vibration parameters obviously contained gross errors; others could be used only after corrections had been applied.\*

We began by checking whether we obtained substantially the same libration amplitudes and frequencies that had been reported for  $-\text{CH}_3$  and  $-\text{NH}_3^+$  groups by Hamilton and his colleagues, who used a somewhat different although essentially equivalent model. We used data from only a few of their structures (listed in the bibliography); for each, our results were the same as theirs within the reported precision. We then analyzed the torsional motion of methyl groups in many other structures determined by neutron diffraction. Several other librating groups were then examined, as discussed below and summarized in Table 1 and Figs. 2 to 5. For a few groups no definitive results could be obtained; possible reasons for this are considered in *Results and discussion*.

Our procedure in analyzing the data was to use the primary information derived from the diffraction experiment, *i.e.* the individual atomic positional and Gaussian ellipsoidal vibration parameters, to derive a mean-square vibration amplitude (MSVA) and a moment of inertia ( $I$ ) for the librating group in question. The moment of inertia was corrected for the effects of libration on interatomic distances, often a substantial correction (as much as 10%). These quantities were then used with the temperature of the experiment (taken to be 296 K if no temperature was stated by the authors, as is frequently the case) in the

\* The most common error is incorrect specification of the form of the anisotropic vibration parameters. Sometimes they are reported to be  $U$ 's when they are manifestly not so; others are given with an incorrect specification of whether or not there is an implicit factor of 2 included with the cross-terms (off-diagonal tensor components, or coefficients of mixed terms in the corresponding quadratic form). This can usually be detected by applying the rigid-bond test for both possibilities, as well as by checking the relative values of the e.s.d.'s of the diagonal and off-diagonal elements (after transformation to  $U$ 's). Normally the e.s.d.'s of the off-diagonal elements should be about 0.7 or 0.8 times those of the diagonal elements (see Hirshfeld & Shmueli, 1972).

calculation of the corresponding harmonic force constant. For a classical harmonic oscillator the force constant,  $f$ , is given by

$$f = kT / \langle \phi^2 \rangle \quad (1)$$

where  $k$  is the Boltzmann constant and  $\langle \phi^2 \rangle$  the MSVA of the motion. If  $f$  is independent of temperature, the MSVA is then proportional to the temperature. However, the classical expression fails at sufficiently low temperature, the MSVA eventually levelling off to a constant value corresponding to the zero-point motion (Fig. 1). The quantum-mechanical expression for  $\langle \phi^2 \rangle$  must then be used in place of (1):

$$\langle \phi^2 \rangle = \frac{h}{8\pi^2 I\nu} \coth \left( \frac{h\nu}{2kT} \right) \quad (2)$$

where  $h$  is Planck's constant,  $\nu$  is the frequency and  $I$  is the moment of inertia\* of the librating group. Expression (2) can be solved for the frequency and the corresponding force constant then obtained from the usual relation,  $f = 4\pi^2 I\nu^2$ . Expression (2) reduces to the classical expression (1) within 1% when the librational frequency in  $\text{cm}^{-1}$  is smaller than about  $0.2T$  (with  $T$  in kelvin), which is true at or near room temperature for almost all the groups examined here except  $-\text{CH}_2$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$ , and  $-\text{NH}_3^+$ .

\* Strictly, the reduced moment of inertia should be used, although it was not in the present calculations. Fortunately, the effect is negligible at the present level of analysis; the classical expression (1), which is independent of  $I$ , applies for almost all of the groups and analyses considered here except those involving the lightest groups ( $-\text{CH}_2$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$  and  $-\text{NH}_3^+$ ) at low temperature or small amplitude. For these groups,  $I$  is so small that the reduced moment of inertia is little different from  $I$  for the group itself.

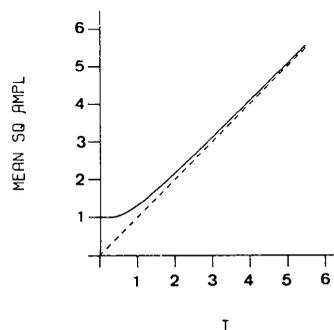


Fig. 1. The solid line is the function  $y = \coth(1/x)$  which shows the variation of mean-square amplitude with temperature for a harmonic oscillator when  $x = 2kT/h\omega c$ . The dashed line is the function  $y = x$ . When the frequency,  $\omega$ , is expressed in  $\text{cm}^{-1}$  and the temperature in Kelvin, the mean-square amplitude is essentially proportional to  $T$  for  $T/\omega$  greater than about 5 (high-temperature portion of the curve), and becomes essentially independent of  $T$ , and equal to  $h/(8\pi^2 I\omega c)$ , when  $T/\omega$  is smaller than about 0.5 (low-temperature portion of the solid curve).

### Limitations

There are clearly many limitations to the kind of analysis we are attempting here. First there is the fundamental difficulty that, given only the atomic vibration tensors, which are sums of mean-square displacements over all vibration modes, there is no unique way of resolving the total vibrational motion into contributions from individual modes. As far as the internal molecular motion is concerned, the best we can do is to postulate the existence of specific kinds of motion and estimate the magnitudes of these motions by including appropriate parameters in the thermal-motion analysis. This kind of approach is guided mainly by chemical intuition, and it can only be expected to give meaningful results where the vibrational motions that are postulated are isolated from other motions affecting the same atoms by a low-frequency separation. This should hold reasonably well for torsional motions of threefold rotors such as methyl groups, less well for certain other kinds of motion, *e.g.* for amino groups where contributions from torsional and inversion modes are both likely to be significant.

We shall discuss the remaining problems briefly under three general headings: the data and librational model, the potential function, and intermolecular effects; some aspects have been reviewed earlier (Trueblood, 1978).

#### *The data and librational model*

Even if the Gaussian-ellipsoidal atomic parameters are precise, they may be inaccurate because of systematic errors arising from absorption, thermal diffuse scattering, or use of too narrow a range of  $\sin \theta/\lambda$  in the diffraction experiment. Systematic errors of these kinds are, however, more likely to be reflected in **T** than in **L** or in the mean-square amplitude of internal libration of a relatively small part of the molecule. Furthermore, although high-amplitude motion (more than about 0.2 to 0.3 rad), which is characteristic of a number of the groups studied here, strains the apparent validity of the quadratic approximations implicit in the **L**, **T**, **S** (Schomaker & Trueblood, 1968) and Dunitz & White (1973) models, these models nevertheless yield amplitudes (Trueblood, 1978) not significantly different from those from more elaborate models employing third-cumulant tensors (Johnson, 1969, 1970) or other higher-order approximations. However, it is clear that least-squares refinement involving the usual six-parameter trivariate Gaussian expression to describe the motion of individual atoms must lead to a loss of information about anharmonicity of the atomic motions.

In addition, the librational model is doubtless oversimplified in its assumption that all of the atomic motions are due either to overall rigid-body molecular

motion or to libration of specific groups about defined directions. Such an assumption ignores other internal modes, such as stretching and bending vibrations, and coupled lattice vibrations. Even for the carbon skeleton of such a 'rigid' molecule as naphthalene, contributions of internal molecular modes to the motions of the atoms in the crystal are by no means negligible (Cyvin, Cyvin, Hagen, Cruickshank & Pawley, 1972). Indeed, at around 100 K the internal out-of-plane vibrations of the naphthalene molecule account for about 40% of the MSVA of the central atoms in the direction normal to the molecular plane (Brock & Dunitz, 1982). Stretching vibrations are particularly important for X-H bonds, as pointed out by Johnson (1970) and Hirshfeld (1976). With the best neutron diffraction data, the mean-square vibration amplitude of an H atom along a C-H bond is of the order of 0.006 to 0.01 Å<sup>2</sup> larger than that of the C atom. Yet we find that without making any correction for this effect we obtain substantially the same torsional amplitudes for methyl or amino groups as are obtained by others after making appropriate corrections. For example, for acetamide at 23 K Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople (1980) made corrections for the C-H and N-H stretching vibrations and then, with Johnson's (1970) segmented-body model, calculated torsional r.m.s. amplitudes for the -CH<sub>3</sub> and -NH<sub>2</sub> groups of 15 and 7°, respectively. Our values, with no such correction included, are 15.1 and 7.6°. If these corrections are unimportant at 23 K and for amplitudes as low as 7°, they should be even less significant for the larger amplitudes characteristic of most -CH<sub>3</sub>, -NH<sub>3</sub><sup>+</sup> and -NH<sub>2</sub> groups at higher temperature. Therefore, we have made no effort to include such corrections.

The problem of coupling between internal and external (lattice) vibrations has been ignored in our work. In principle, this problem could be handled by appropriate lattice-dynamical calculations, but at the present stage these are hardly possible for most of the kinds of molecules considered here (see Gavezzotti & Simonetta, 1982). In our simple model, the molecular **L**, **T** and **S** tensors (evaluated routinely in our analyses, although not discussed explicitly in the present work) are identified with the external 'rigid-body' motion to which the internal contributions are added.

#### *The potential function*

Anharmonicity of the potential function not only clouds the interpretation of the **L**, **T** and **S** tensors and of our derived internal torsional amplitudes, all based on the harmonic approximation, but it also vitiates attempts to calculate a force constant with equations (1) or (2) from the mean-square amplitude  $\langle \varphi^2 \rangle$ . We were tempted merely to plot  $RT/\langle \varphi^2 \rangle$ , a quantity that could be identified with the classical quadratic force constant per mole [equation (1)]. However, this would

be inappropriate for the low-temperature studies of groups with the lowest moments of inertia, where the value of the quadratic force constant derived from (2) can be as much as ten times the classical value given by (1). Consequently, we assumed harmonic-oscillator behavior and used equation (2) to obtain the quadratic force constants, which are plotted in Figs. 2 to 5 and listed in Table 1.

If one wishes to calculate a barrier from the force constant, further uncertainties are introduced. The shape of the actual potential is, of course, unknown. A common procedure is to assume the simplest periodic potential consistent with the rotational symmetry of the librating group:

$$V = B(1 - \cos n\varphi)/2. \quad (3)$$

$B$  is the potential barrier, *i.e.* the height at  $\varphi = \pi/n$  relative to that at  $\varphi = 0$ . For small  $\varphi$ , we may expand  $\cos n\varphi$  as a power series and neglect all terms beyond quadratic to obtain

$$V = Bn^2\varphi^2/4 = f\varphi^2/2, \quad (4)$$

so that the barrier  $B$  can be related to the quadratic force constant  $f$  by

$$B \sim 2f/n^2 \quad (5)$$

or

$$B \sim 2kT/n^2\langle\varphi^2\rangle \quad (6)$$

in the classical approximation. The error in  $V$  introduced by using (4) instead of (3) to represent the potential is less than 5% for  $n\varphi$  as large as 0.77 rad.

What about the error in the estimation of the force constant  $f$  from an expression such as (1) when the potential is not harmonic? For the periodic potential (3) a classical Boltzmann averaging gives for  $\langle\varphi^2\rangle$  at temperature  $T$ :

$$\begin{aligned} \langle\varphi^2\rangle &= \frac{\int_0^{\pi/n} \varphi^2 \exp[-B(1 - \cos n\varphi)/2kT] d\varphi}{\int_0^{\pi/n} \exp[-B(1 - \cos n\varphi)/2kT] d\varphi} \\ &= \frac{\int_0^{\pi} \alpha^2 \exp[A \cos \alpha] d\alpha}{n^2 \int_0^{\pi} \exp[A \cos \alpha] d\alpha} \quad (7) \end{aligned}$$

where  $\alpha = n\varphi$  and  $A = B/2kT$ . Numerical integration of (7) shows that  $\langle\varphi^2\rangle \sim 1/An^2$  or  $A \sim 1/n^2\langle\varphi^2\rangle$  [compare (6)] with an error of less than 10% for  $An^2 \geq 6$ .

Thus, to the extent that one can assume a sinusoidal potential of the form given by (3), and provided the classical approximation holds, equation (5) should be

more than good enough for our purpose when  $An^2 > 6$ , *i.e.* when the barrier  $B$  exceeds  $12kT/n^2$  or when the mean-square librational amplitude is smaller than about  $0.17 \text{ rad}^2$  (r.m.s. amplitude  $< 24^\circ$ ). In the small-barrier or high-temperature limits, force constants estimated from (1) or (2) and barriers estimated from (6) will be somewhat too low. The other uncertainties, including in many structures the estimates of mean-square libration amplitudes themselves, are usually more serious. Nevertheless, the assumptions implicit in using (5) should always be kept in mind: that the potential is periodic with only a single dominant term (of known  $n$ ), and that the amplitude is sufficiently small that the deviation from harmonic behavior is not serious.

As an extreme deviation from harmonic behavior, large vibration parameters could be due to disorder in the crystal structure as well as to genuine vibration. The two types of behavior are distinguishable, in principle, by temperature-dependent measurements, or possibly by inclusion of third and fourth cumulants in the structure refinement, but for only very few of the structures included in our study were these additional kinds of information available. Our interpretation of the vibration parameters as arising exclusively from genuine vibration may therefore be in error for large apparent vibration amplitudes and this means that force constants and torsional barriers in the low range may be questionable. (Force constants and torsional barriers in the high range are associated with large relative uncertainties because they are based on small MSVA's which, *ceteris paribus*, are relatively less accurate than large ones.)

#### Intermolecular effects

There are also some serious problems connected with the very nature of the crystalline state: the influence of *intermolecular* effects on *intramolecular* torsions. According to Fateley, Harris, Miller & Witkowski (1965), torsional frequencies are typically some 20 to 25% higher in liquids than in the gas phase, which implies that force constants will be about 50% higher in liquids. This is clearly at best a very rough guideline; for very bulky groups, or for polar groups that might interact strongly with others in nearby molecules, even larger effects might be expected. One might anticipate still further increases in force constant on going to the crystalline state since the packing coefficients (which reflect the densities) of typical organic crystals are usually 10 to 20% greater than those of the corresponding liquids (Kitaigorodsky, 1973).

Thus one might expect a spread of calculated  $f$  values for a given group in different crystals, with the lowest values not far above those found in the gas phase by other methods, especially for small non-polar groups. The highest  $f$  values for a given group,

corresponding to the smallest amplitudes at a particular temperature and having the largest relative error, are of more questionable significance, although they presumably reflect, at least in part, environmental effects.

In any particular crystal, however, we do not know to what extent the observed force constant is an intrinsic property of the molecule and to what extent it is influenced by intermolecular forces. Given the crystal structure, this question could be studied in principle by appropriate force-field calculations, but that would be a problem for itself and one that we shall not discuss here. We merely note that Afonina & Zorkii (1976) have calculated the variation of intermolecular potential energy for methyl-group rotation in a variety of crystalline compounds and estimated barriers that vary from about 1 to more than 40 kJ mol<sup>-1</sup>.

### Results and discussion

Table 1 summarizes the results for most of the torsional librations studied. The individual harmonic force constants for the groups that comprised the bulk of the cases investigated in the many different structures are plotted in Figs. 2 through 5; because of space

limitations the individual values for the other groups listed in Table 1 have not been plotted, but a few of them are discussed below. Table 1 includes the range of force-constant values found for each group in the different structures (identified by numbers in Table 1 or in the appropriate figure), the corresponding barrier for a specified  $n$ , and some relevant literature values, with references. The average of the force constants is included as well for the methyl and trifluoromethyl groups only. Even for these groups the average is of dubious significance because of varying environmental influences. For the other groups, an average was considered more misleading than helpful.

We discuss the results for each group in turn, with a few comments at the end about groups not included in Table 1.

#### Methyl

Fig. 2 shows force constants for more than 60 methyl groups on trigonal and tetrahedral C, N and P atoms. The range of  $f$  values found for methyl on O (six structures, 17 values) is given in Table 1, but no plot is shown.

The first eleven points on the left of Fig. 2 are for methyl groups on aromatic C or N atoms; all but six of

Table 1. Summary of harmonic torsional force constants and equivalent cosine-function potential barriers

Group	Attached atom	Structures*	Force constant (J mol <sup>-1</sup> deg <sup>-2</sup> )		Barrier (kJ mol <sup>-1</sup> )		Relevant literature values			
			Range	Ave. (e.s.d.)	Range	Ave.†	Molecule or attached atom	Phase§	Barrier (kJ mol <sup>-1</sup> )	References
-CH <sub>3</sub>	C, N trig.	See Fig. 2	2.0-13.1	5.6 (2.4)	V <sub>3</sub> = 1.5-9.6	4.1	C aromatic	s	V <sub>3</sub> = 1.2-8.5	a, b, c
	C, N, P tetr.	See Fig. 2	5.3-35	15.6 (7.4)	V <sub>3</sub> = 4-26	11	Other C trig.	g	V <sub>3</sub> = 3-11	d
	O	10, 40, 43, 44, 49, 51	1.4-12	5.2 (3.1)	V <sub>3</sub> = 1-9	4	C tetr.	g	V <sub>3</sub> = 12-22	d, e
-NH <sub>2</sub>	C	13, 24, 37, 42, 62, 79	19-85		V <sub>3</sub> = 14-62		CH <sub>3</sub> OH	g	V <sub>3</sub> = 4.5	f
		Other					C	s	V <sub>3</sub> = 15-19	g, h
-NH <sub>2</sub>	C trig.	1, 10, 12, 13, 47, 48, 62, 80, 92, 93	24-245		V <sub>2</sub> = 40-400		Formamide, substituted amides, dimethylamino-pyrimidines	l	E <sub>A</sub> = 75	j
								l	G  = 67-92	k
									<32-59	l
-CF <sub>3</sub>	C tetr.	12	9		V <sub>3</sub> = 7					
	C trig.	See Fig. 3	5.6-13.3	9.9 (3.0)	V <sub>3</sub> = 4-10	7	C trig.	g	V <sub>3</sub> = 4-7	d, m
	C tetr.	See Fig. 3	13-91	34 (22)	V <sub>3</sub> = 9-66	25	C tetr.	g	V <sub>3</sub> = 13-25	d, n, o
-C(CH <sub>3</sub> ) <sub>3</sub>	C, N trig.	See Fig. 4	19-149		V <sub>3</sub> = 14-109		C trig.	g	V <sub>3</sub> = 2 to >10	e, p
	C, N*, P tetr.	See Fig. 4	9-154		V <sub>3</sub> = 7-112		C tetr.	g	V <sub>3</sub> (calc.) = 17-27	q
	C aromatic	See Fig. 5	17-85		V <sub>2</sub> = 28-140		C aromatic	g	V <sub>2</sub> = 12-20	r, s, t
-NO <sub>2</sub>	C tetr.	See Fig. 5	4.4-55		V <sub>2</sub> = 7-90		Other C trig.		20-31	u, v
							CH <sub>3</sub> NO <sub>2</sub>		V <sub>6</sub> = 0.03	f
Nitrocyclopropane								V <sub>2</sub> = 13	w	
-CO <sub>2</sub> <sup>-</sup> , -COOH	C	See Fig. 5	15-116		V <sub>2</sub> = 25-190					
-CCl <sub>3</sub>	C, P, S	20, 21, 46, 56, 61, 63, 65	21-263		V <sub>3</sub> = 15-192		C tetr.	l	V <sub>3</sub> = 25-70	x
-OCH <sub>3</sub>	C aromatic	11, 82, 83, 86, 94, 95, 96, 97	9-76		V <sub>2</sub> = 15-125		C aromatic	g	V <sub>2</sub> = 4-15	y
								l, s	25-37	z

References: (a) Kanesaka, Naka & Kawai (1979). (b) Hamilton, Edmonds, Tippe & Rush (1969). (c) Rush (1967). (d) Lowe (1968). (e) Durig, Craven, Mulligan, Hawley & Bragin (1973). (f) Cited by Lister, MacDonald & Owen (1978). (g) Durig, Player, Bragin & Li (1971). (h) Durig & Brown (1976). (i) Ratcliffe & Dunell (1978). (j) Sunners, Piette & Schneider (1960). (k) Yoder & Gardner (1981). (l) Riand, Chenon & Lumbroso-Bader (1980). (m) Durig & Church (1980). (n) Bürger, Niepel & Pawelke (1980). (o) Kalasinsky & Anjaria (1980). (p) Thomas, True & Bohn (1980). (q) Baas, van de Graaf, van Veen & Wepster (1980). (r) Høg, Nygaard & Sørensen (1971). (s) Correll, Larsen & Pedersen (1980). (t) Ralowski & Ijunggren (1977). (u) Meyer, Gammeter, Smith, Kühne, Nösberger & Günthard (1973). (v) Caminati (1982). (w) Mochel, Britt & Boggs (1973). (x) Allen & Fewster (1974, cited on p. 268). (y) Owen & Hester (1969). (z) Allen & Fewster (1974, cited on p. 275).

\* Structure reference numbers are given in the bibliography (Table 2).

† Average values are given only for -CH<sub>3</sub> and -CF<sub>3</sub> (see text).

§ g, gas; l, liquid or liquid solution; s, solid.

‡ Quoted barriers for -NH<sub>2</sub> vary widely with environment, an effect discussed by Jones, Bernal, Frey & Koetzle (1974) and investigated also by Ratcliffe & Dunell (1978) and attributed chiefly to variation in hydrogen-bonding strength.

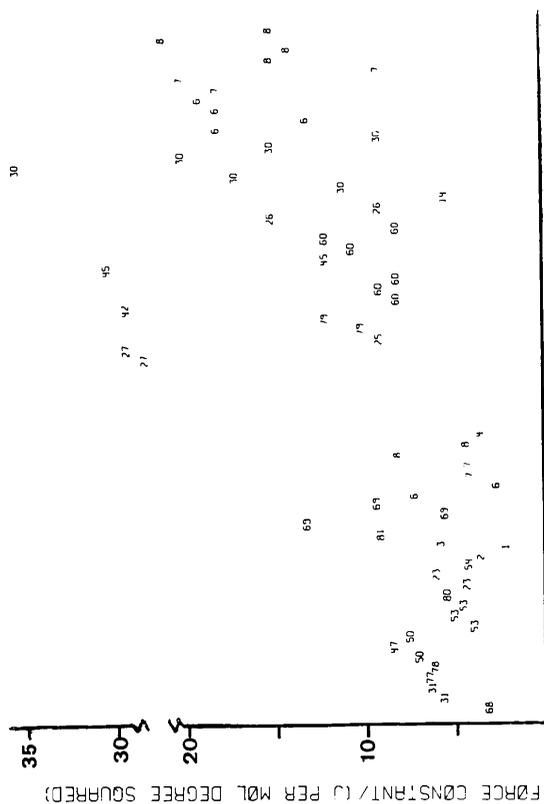


Fig. 2. Harmonic force constants for libration of methyl groups on trigonal C and N (left group) and on tetrahedral C, N and P (right group). The numbers designate the structures listed in the bibliography (Table 2).

the remaining points in the left group (those for structures 6, 7 and 8) are for acetyl methyls. The  $f$  values for the aromatic methyls range from 3.0 to 8.3 (average 5.7)  $\text{J mol}^{-1} \text{deg}^{-2}$ , corresponding to a barrier  $V_3$  ranging from 2.2 to 6.1  $\text{kJ mol}^{-1}$ . Literature values for analogous  $V_3$  barriers in solid phases cover a similar although slightly wider range (Table 1). (The barrier to methyl rotation in gaseous toluene,  $V_6$ , is about 0.05  $\text{kJ mol}^{-1}$ .) For the other methyls on trigonal C, the  $f$  values range from 2.0  $\text{J mol}^{-1} \text{deg}^{-2}$  (in acetamide, excellent data) to 13.1  $\text{J mol}^{-1} \text{deg}^{-2}$ , and the corresponding  $V_3$  barriers (1.5 to 9.6  $\text{kJ mol}^{-1}$ ) again cover a range comparable to, although somewhat lower than, that reported for a variety of similar gaseous compounds, as indicated in Table 1. We found no appropriate references to studies on crystalline phases; however, the range of values reported for the gaseous compounds is so broad that we would not expect it to change appreciably because of the change of phase. We conclude that for methyl groups on trigonal atoms, the present method gives results that are quite comparable with and of the same order of magnitude as those given by other methods.

The methyl group in acetamide, one of the most accurate structures at our disposal (neutron diffraction, 23 K), is rotated by about  $30^\circ$  from the stable conformation of the free molecule (Jeffrey *et al.*, 1980). This shows that packing forces may alter the position

of torsional equilibrium and reminds us that low barriers may be due to raising of the ground state as well as to lowering of the transition state.

Fig. 2 shows that the  $f$  values obtained for methyl on tetrahedral C, N and P are on the whole appreciably larger than those on trigonal atoms, consistent with the greater  $V_3$  barriers reported for such groups (12–22  $\text{kJ mol}^{-1}$ , Table 1). We find the average  $V_3$  barrier for methyl on a tetrahedral atom to be nearly three times as large as on a trigonal atom, but somewhat surprisingly we find many individual methyl groups on tetrahedral C (and P) with  $V_3$  barriers significantly below the lowest reported gas-phase value (12  $\text{kJ mol}^{-1}$ ). For example, Fig. 2 shows 14  $f$  values in the range 8 to 12  $\text{J mol}^{-1} \text{deg}^{-2}$ , corresponding to  $V_3$  barriers in the range 6 to 9  $\text{kJ mol}^{-1}$ . One further structure (14) has an even lower  $f$  value. There may be some unrecognized systematic error which is responsible for these low values, but we tend to think they are genuine.

The highest  $f$  values in Fig. 2 are in a cluster of five near 30  $\text{J mol}^{-1} \text{deg}^{-2}$ . At least one of them is suspect; the data for structure 30 are of low quality by the rigid-bond test. Three of the other four values are for methyl on  $\text{N}^+$ ; the other is for the methyl group in L-alanine (structure 42), for which the data are of high quality.

Seventeen methyl groups on O atoms were studied, nine in structure 40 and two on independent methanol molecules in structure 43. The apparent r.m.s. librational amplitudes for the latter are so high (31 and  $40^\circ$ ) that the corresponding barriers (1.5 and 1.1  $\text{kJ mol}^{-1}$ ) must be taken *cum grano salis*. However, three of the nine independent methyls on phosphite O atoms in structure 40 give comparable barriers from distinctly lower amplitudes and lower temperature (measurements at 90 K), although the average for all nine is 3.0 (1.7)  $\text{kJ mol}^{-1}$ . The average of all the  $\text{CH}_3\text{—O}$  barriers, including these low ones, is a little above 5  $\text{kJ mol}^{-1}$ , slightly above the reported barrier of 4.5  $\text{kJ mol}^{-1}$  for gaseous methanol but distinctly below the range of 15–19  $\text{kJ mol}^{-1}$  reported (Table 1) for  $\text{CH}_3\text{—O}$  barriers in some crystalline methyl ethers and methyl esters studied by far-infrared spectroscopy. We have not tried to assess the possible significance of this difference, nor to advance explanations for it.

#### Ammonio

Barriers found for the  $\text{—NH}_3^+$  group attached to C atoms are far higher than those for methyl groups, as others also have observed (see footnote to Table 1). It seems eminently plausible to attribute this difference to interactions of the  $\text{—NH}_3^+$  group with surrounding anions and polar groups. The one neutron diffraction study of an  $\text{—NH}_3^+$  group attached to O (hydroxyl-ammonium perchlorate (Prince, Dickens & Rush,

1974), not included in Table 1] presents, as Speakman (1975) has noted, a striking contrast. The r.m.s. torsional amplitude of the  $-\text{NH}_3^+$  group for each of two crystallographically independent molecules is about  $25^\circ$ , corresponding to a harmonic force constant of about  $4 \text{ J mol}^{-1} \text{ deg}^{-2}$  and a barrier of about  $3 \text{ kJ mol}^{-1}$ , an astonishingly low value for a polar group in an ionic environment. Prince *et al.* attribute the large torsional amplitude to the fact that hydrogen-bonding opportunities are more or less continuously available as each  $-\text{NH}_3^+$  group rotates about its N—O axis. Some of the individual hydrogen bonds are short and presumably fairly strong; the weaker ones are bifurcated. It may be relevant that in the crystalline complex of 18-crown-6 with hydroxylammonium perchlorate (Trueblood, Knobler, Lawrence & Stevens, 1982), the  $-\text{NH}_3^+$  group is disordered and forms bifurcated hydrogen bonds, in marked contrast to the situation in the corresponding hydrazinium and methylammonium complexes. Because these were X-ray structure determinations, no librational amplitudes could be calculated for the  $-\text{NH}_3^+$  groups.

#### Amino

We examined the motion of this group in five amides, for all of which the data are of good to excellent quality (structures 1, 13, 80, 92, 93), and in a number of other structures as well (Table 1). In most of these structures, the amino group is part of a conjugated system and coplanar with it. In such situations, torsion about the N—C bond and out-of-plane bending at the N atom both produce motions of the H atoms in the direction normal to the reference plane, and hence the two types of vibration cannot be distinguished from one another on the basis of the atomic vibration tensors alone. For all these amino groups we have arbitrarily analyzed the combined motion as if it were a pure torsional motion. The derived force constants and rotational barriers are therefore somewhat artificial, but at least they could be regarded as lower limits.

The force constants for the amide structures range from 63 to  $201 \text{ J mol}^{-1} \text{ deg}^{-2}$ , corresponding to barriers  $V_2$  between about 100 and  $330 \text{ kJ mol}^{-1}$ . Even if these are lower limits, they are nevertheless larger than the activation energies determined by NMR methods for rotation about the C—N bond in various amides in solution, which cluster around  $80 \text{ kJ mol}^{-1}$ . However, since there is strong hydrogen bonding in all of the crystals, we expect barriers higher than those in solution. The values found thus seem to be of the right order of magnitude, but since the estimated errors in most of them approach 50% (the amplitudes are generally rather low) any further discussion must await a more extensive study.

For amino groups on aromatic C atoms (seven values, structures 10, 47, 48 and 62) we find  $f$  values

ranging from 24 to  $245 \text{ J mol}^{-1} \text{ deg}^{-2}$ , corresponding to barriers  $V_2$  between about 40 and  $400 \text{ kJ mol}^{-1}$ . The lower limit of this range is in reasonable accord with literature values (Table 1); we place little credence in the values near the higher end of the range.

The one example of an amino group on a tetrahedral C atom (in arginine dihydrate) has a force constant of  $9 \text{ J mol}^{-1} \text{ deg}^{-2}$ , far lower than any of those on a trigonal atom, and consistent with the expected loss of double-bond character in the C—N bond. The value is, in fact, quite comparable to that of a methyl group on a tetrahedral atom (Table 1).

#### Trifluoromethyl

The results for this group, plotted in Fig. 3, resemble those for the methyl group, although the absolute values of the force constants are somewhat greater and there are only about one third as many examples. The  $f$  values for  $\text{CF}_3$  attached to trigonal atoms (left cluster) are typically distinctly smaller than for those attached to tetrahedral atoms, quite in accord with what has been reported earlier for gaseous compounds in these two classes. Again the values we find seem clearly of the right order of magnitude; since the data are only fair (by the rigid-bond test) at best and even rather poor

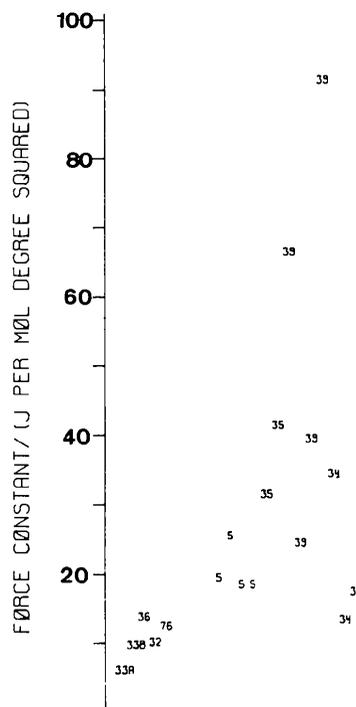


Fig. 3. Harmonic force constants for libration of trifluoromethyl groups on trigonal C (left group) and tetrahedral C (right group). The numbers designate the structures listed in the bibliography (Table 2).

for the majority of the compounds, further analysis of individual values is not warranted at present.

#### *tert-Butyl*

For this relatively bulky group we expect that intermolecular and intramolecular steric effects should have a significant effect on the torsion potential so that the chemical nature of the atom to which the group is attached should no longer be a dominant factor. Fig. 4 shows the results for *tert*-butyl and (on the extreme right) three similar groups. There is no obvious difference in torsional force constant for groups attached to trigonal and to tetrahedral atoms. Although many of the data sets are of low quality, so that conclusions must be tentative, it is interesting that the values at the lower end of the range for each kind of attached atom are of the right order of magnitude in comparison with values determined or calculated for gaseous molecules (see Table 1). Whether the much higher values found for some of the groups in certain structures can be reconciled with their inter- and intramolecular environments in even a semiquantitative way awaits more careful measurements and more detailed analysis.

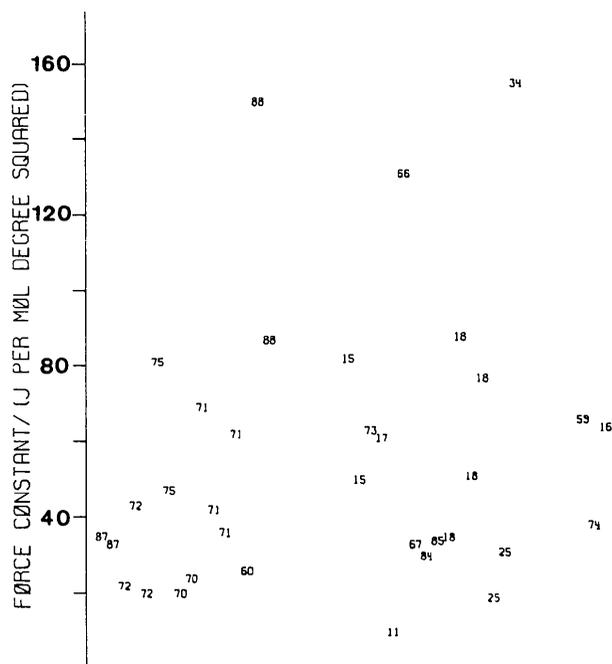


Fig. 4. Harmonic force constants for libration of *tert*-butyl groups on trigonal C and N (left group) and on tetrahedral C, N and P (center group), and for libration of groups similar to *tert*-butyl [right group of three;  $(\text{CH}_3)_3\text{X}$ -, with  $\text{X} = \text{Si}, \text{P}$  and  $\text{N}$ ]. The numbers designate the structures listed in the bibliography (Table 2).

#### *Nitro and carboxy groups*

For these two groups, the torsional motion is likely to be much more important than out-of-plane bending at the trigonal atoms. We have therefore analyzed the combined motion as if it were pure torsion (as for the amino group discussed earlier but with more justification). Results are presented in Fig. 5 and summarized in Table 1. Unfortunately, the data are at best fair and often poor. For the nitro group on aromatic C (the left group of fifteen points) the lowest  $f$  values are quite consistent with one another, and the corresponding barriers are nearly twice the average value reported for comparable gaseous molecules. Thus they are again of the right order of magnitude and differ from the gas-phase values in the expected direction. Two of the three highest values found are for highly hindered nitro groups, which is reassuring.

The central group of 11 points in Fig. 5 refers to nitro groups on quaternary substituted C atoms. The lowest value (structure 57) corresponds to a barrier  $V_2$  of about 7 kJ mol<sup>-1</sup>, which seems suspiciously low. The others range upward from  $V_2$  of about 16 kJ mol<sup>-1</sup>. The  $V_2$  barrier of 39 kJ mol<sup>-1</sup> for the C-NO<sub>2</sub> bonds in 1,1'-dinitrobicyclopropyl (structure 90) has been discussed by Kai *et al.* (1982) in terms of the preference of the nitro group, as a powerful  $\pi$ -electron acceptor, for a

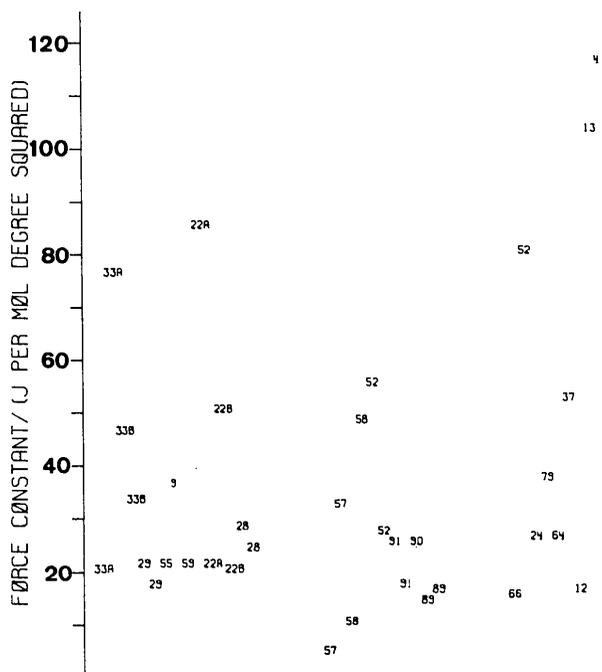


Fig. 5. Harmonic force constants for libration of nitro groups on aromatic C (left group) and tetrahedral C (center group) and for libration of carboxylate and carboxy groups on C (right group). The numbers designate the structures listed in the bibliography (Table 2).

particular (so-called bisected) conformation with respect to the cyclopropane ring. For gaseous nitro-cyclopropane the analogous conformation has been found by microwave spectroscopy with a  $V_2$  barrier of 13 kJ mol<sup>-1</sup> (Table 1); however, the reported uncertainty in this barrier is nearly 50%. Also, the change from a tertiary to a quaternary substituted C atom seems more likely to increase the force constant than to decrease it.

The force constants for carboxy and carboxylate groups cover a broad spectrum, not surprisingly in view of the possibilities of hydrogen bonding and other polar interactions. The values shown in Fig. 5 (right group of nine points) are with one exception for groups on aliphatic C. The exception (structure 66, aromatic C) is the one with the lowest force constant. We found no appropriate literature values for comparison.

### *Trichloromethyl*

We found no data of good quality for structures containing this group, so the results do not warrant detailed analysis. The lowest  $f$  value, corresponding to  $V_3 = 15$  kJ mol<sup>-1</sup>, should be discounted, since only a small part of the structure (56) was refined anisotropically. The other barriers range upward from about 30–35 kJ mol<sup>-1</sup>, consistent with literature values (Table 1).

### *Methoxy*

For methoxy substituents on aromatic rings we attempted to estimate libration amplitudes of the methyl group about the C(ar.)–O bond. Data are available for many such compounds, but the results were erratic on the whole, partly because this internal torsional motion could seldom be well resolved from overall rigid-body molecular libration about a direction not far from that of the C–O axis. Only for the spherands (Cram & Trueblood, 1981) and related molecules was any sort of consistency obtained; these large molecules have quite rigid frameworks and comparatively little overall motion in the crystals. Although some of the data are not of high quality, more than twenty  $f$  values could be estimated, about half of which lie in the range 9 to 24 J mol<sup>-1</sup> deg<sup>-2</sup>. These correspond to torsional barriers  $V_2$  between about 15 and 39 kJ mol<sup>-1</sup>, quite comparable to the values found by other methods in liquid and solid phases (Table 1).

### *Bending motions*

Scrutiny of the patterns of atomic vibration parameters suggests that in some molecules bending or

wagging motions, rather than torsional oscillations about bond directions, are important. For example, many spherands and hemispherands contain methyl groups attached to aromatic rings, with the methyl C atoms showing distinctly greater vibration amplitude normal to the ring plane than in this plane and normal to the exocyclic bond. We have analyzed this extra motion in terms of an out-of-plane bending of the methyl C atom about an axis lying in the aromatic ring plane and passing through the substituted ring atom, normal to the exocyclic bond. The force constants obtained for this motion in 18 examples ranged from 9 to 169 J mol<sup>-1</sup> deg<sup>-2</sup> with half between 21 and 48 J mol<sup>-1</sup> deg<sup>-2</sup>. The corresponding out-of-plane bending force constant for several valence force fields of benzene (Bürgi & Shefter, 1975) is about 70 J mol<sup>-1</sup> deg<sup>-2</sup>, well within the tolerance of our estimates.

In another somewhat similar application, we found that for at least one structure based on accurate low-temperature X-ray data, the incipient internal motion corresponding to the N-inversion process could be detected without difficulty from the generalized rigid-bond test. The structure in question (1,8,11-trimethyl-11-aza-9,10-benzopentacyclo-[6.2.1.0<sup>2,6</sup>.0<sup>2,7</sup>.0<sup>3,7</sup>]undec-9-ene) was determined at 95 K to obtain accurate deformation density maps (Chakrabarti, Seiler, Dunitz, Schlüter & Szeimies, 1981) and the e.s.d.'s of the diagonal elements of the atomic vibration tensors are only about  $7 \times 10^{-4}$  Å<sup>2</sup>. At 95 K the heavy-atom skeleton of the molecule behaves as a rigid body except for the N-methyl group which vibrates manifestly more along the coordinate leading to N inversion than normal to this direction. If this motion is simulated as a torsion about an axis passing through the N atom we obtain for it a force constant of 170 (50) J mol<sup>-1</sup> deg<sup>-2</sup>.

### *Other groups*

We had hoped to study possible torsion motions about purely olefinic bonds but found no suitable data. However, two neutron diffraction structures of olefins coordinated to metal atoms were examined. For ethylene coordinated to Pt in Zeise's salt (structure 41), force constants of 30 and 38 J mol<sup>-1</sup> deg<sup>-2</sup> were obtained for the twisting of the two crystallographically independent methylene groups about the C–C axis. In structure 19, which has a vinyl group coordinated to a triangle of Os atoms, the much higher  $f$  value of 114 J mol<sup>-1</sup> deg<sup>-2</sup> was found for the torsion of the methylene group. In these structures, the C–C bond is lengthened from its value in ethylene by about 0.04 and 0.06 Å, respectively, and the atoms of the olefinic moiety are no longer coplanar, so there has evidently been some diminution of double-bond character in the C–C bond. However, it is unclear what force constants are to be expected for these motions. In any

case, further analysis of olefinic compounds seems warranted when suitable neutron diffraction data are available.

There have been several precisely determined neutron diffraction structures of urea and guanidinium derivatives, but most of our attempts to determine amino-group librational amplitudes in these molecules led to widely divergent – sometimes even negative – values. For small molecules, or those undergoing extensive overall librational motion, or for groups on the periphery of large molecules that are librating even moderately, resolution of internal motion from overall motion becomes difficult with obvious detrimental consequences for our method of analysis. The results of attempts to analyze the motion of dimethylamino groups (in amides or as substituents on aromatic nuclei) were sufficiently erratic that we do not report them here, although some such analyses have been moderately successful.

An example is provided by the room-temperature X-ray structure of 8-hydroxy-*N,N*-dimethylnaphthalene-1-carboxamide (Schweizer, Procter, Kaftory & Dunitz, 1978) where the rigid-body test is satisfied quite well except for one atom, the C atom of the dimethylamino group that is *anti* to the amide O atom. Two models involving different types of non-rigid motion gave almost equally satisfactory results. Model 1 involved a torsional vibration of the entire amide group about the exocyclic C–C bond and gave an r.m.s. amplitude of  $4.9 (6)^\circ$  for this motion. Model 2 involved motion only of the egregious C atom out of the plane of the amide group; this was simulated by a suitable torsion with the motion imparted only to this atom [r.m.s. amplitude  $9.1 (1.3)^\circ$ ]. The actual motion may be a combination of these. Model 2 is analogous to the N-inversion process in nonplanar enamines, which involves mainly a motion of the N substituent *anti* to the double bond (Brown, Damm, Dunitz, Eschenmoser, Hobi & Kratky, 1978).

### Conclusions

Force constants and potential barriers for torsional motions of various chemical groups estimated from atomic vibration parameters derived from single-crystal X-ray and neutron diffraction data are found to be in reasonable agreement with values measured by other techniques, mostly for molecules in the gas phase. The relative paucity of high-quality data has meant that the examples included in the present study have had to be chosen primarily for their availability. This has prevented us from making as systematic a study as we might otherwise have wished. Nevertheless, the structures analyzed here present many opportunities for checking the internal consistency of the method, or, alternatively, for using the approach as a probe of intermolecular and intramolecular potential functions. To exploit these

opportunities properly would involve detailed analyses of the intermolecular and intramolecular environment of each group being considered, analyses that we have not even begun to make. Since our present objective has been only to assess the potentialities of the method, we merely draw attention to a few salient features of the structures examined and point to directions in which further work seems to be needed.

(1) Several of the structures contain molecules with two or more groups that are chemically but not crystallographically equivalent. To the extent that their intermolecular environments in the crystal are similar, one would expect similar libration amplitudes and force constants. For example, durene (structure 31) and its *tert*-butyl analog (structure 70) each contain two groups of this kind. The force constants are indeed quite similar for the two groups in each of these structures, as shown in Figs. 2 and 4. When the force constants in structures of this kind are significantly different, with due allowance for the precision of the estimates (*e.g.* for structure 69, Fig. 2), the differences should be rationalizable in terms of the intermolecular environments. (2) A number of the structures contain chemically identical but crystallographically independent molecules (identified by the letters *A* and *B* in the figures). Such structures provide further opportunities to assess the effect of the intermolecular environment since this differs for the two molecules. (3) In many of the structures, a given molecule contains several groups of the same kind in differing intramolecular (as well as intermolecular) environments. Analyses of these structures will necessarily be more complicated, but an eventual aim must be the reconciliation of the derived force constants with intermolecular and intramolecular potential functions.

Since no other available method is free from significant limitations in scope or precision, the present method seems to offer a valuable complement to other methods of studying torsional and similar relatively soft intramolecular motions. It seems likely that it will come into more general use in future. The number of highly precise and accurate structures is almost certain to increase greatly in the next decade, so it should soon be possible to analyze in more detail and in a more systematic manner the variations in torsion barriers among similar groups in different environments. Studies of polymorphic forms should be especially valuable for probing intermolecular potentials.

One omission that should be made good is the paucity so far of temperature-dependent studies of structures containing librating groups.\* Since the

\* Apart from the X-ray study of triclinic ferrocene at 100, 125, and 150 K (Seiler & Dunitz, 1979) where force constants were estimated for libration of the molecules about their fivefold axes at each temperature. See also Seiler & Dunitz (1980) for the possibility of resolving the motion into libration of the individual cyclopentadienyl rings.

Table 2. Bibliography

1. ACEMD03 ACETANIDE (N) G.A.JEFFREY ET AL, ACTA CR., B36,2292,1980.
2. ACETAC03 ACETIC ACID (133 K) (N) P.-G.JONSSON, ACTA CR., B27,893,1971.
3. ACNITR20 CHLOROACETIMINIUM CHLORIDE (268 K) (N) J.M.WILLIAMS ET AL, INORG.CH., 7,2577,1968.
4. ACYGLV11 N-ACETYLYLGLYCINE (N) M.F.MACKAY, CR.STR.COMM., 4,225,1975.
5. AFM1Z0 4-AMINO-2,5,5-TETRAKIS (TRIFLUOROMETHYL)-3-IMIDAZOLINE L.J.GUGGENBERGER,ACTA CR., B29,2110,1973.
6. AMBONCO1 BIS(2-AMINO-2-METHYL-3-BUTANONE OXIMATE) NICKEL(II) CHLORIDE MONOHYDRATE (N) E.O.SCHLEMPER,W.C.HAMILTON,S.J.LA PLACA, J.CHEM.PHYS., 54,3990,1971.
7. AMBONI1 BIS(3-AMINO-3-METHYL-BUTAN-2-ONE-OXIMATE)-NICKEL(II) CHLORIDE MONOHYDRATE (N) B.HSU,E.O.SCHLEMPER,C.K.FAIR, ACTA CR., B36,1387,1980.
8. AMBXP10 BIS(2-AMINO-2-METHYL-3-BUTANONE OXIMATE) PLATINUM(II) CHLORIDE HYDRATE (N) E.O.SCHLEMPER,C.K.FAIR, ACTA CR., B33,2482,1977.
9. AMNTPY 2-AMINO-3-NITROPYRIDINE R.DESTRO ET AL, ACTA CR., B31,2803,1975.
10. AMXBPM10 2,4-DIAMINO-5-(3,4,5-TRIMETHOXYBENZYL)PYRIMIDINE (N) T.F.KOETZLE ET AL, J.AM.CHEM.SOC., 98,2074,1976.
11. ANCRBA TRIANISYL-CROWN T-BUTYLAMMONIUM PERCHLORATE (113 K) K.N.TRUEBLOOD ET AL, AM.CR.ASSOC.,SER.2, 6,57,1979.
12. ARGIND11 L-ARGININE DIHYDRATE (N) M.S.LEHMANN ET AL, J.CHEM.SOC.,PERKIN 2, 133,1973.
13. ASPARM02 L-ASPARAGINE MONOHYDRATE (N) J.J.VERBIST ET AL, ACTA CR., B28,3006,1972.
14. ASYTHS01 NONA-AQUO-YTTRIUM(III) TRIS(ETHYL-SULFONATE) (110 K) (N) R.W.BROACH ET AL, ACTA CR., B35,2317,1979.
15. BEHMH0 2,6-DI-T-BUTYL-5,6-EPOXY-2,4-DIHYDROXY-4-METHYL-1,3-HEXANEDIONE P.RAFFERTY ET AL, ACTA CR., B35,2067,1979.
16. BMSINA T-BUTYL-DIMETHYLSILOXY-ACI-NITROPHENYLMETHANE (101 K) E.W.COLVIN ET AL, HELV.CHIM.ACTA, 63,697,1980.
17. BPPOHY TRANS-4-T-BUTYL-1-PHENYLPHOSPHORINANE OXIDE G.D.MACDONELL ET AL, J.AM.CHEM.SOC., 100,4535,1978.
18. BUCVPS TETRA-T-BUTYLCYCLOTRIPHOSPHANE W.WEIGAND ET AL, ACTA CR., B37,1631,1981.
19. CHVINO DECARBONYL-MU-HYDRIDO-MU-VINYL-TRIANGULO-TRI-OSMIUM (N) A.G.ORPEN ET AL, ACTA CR., B34,2466,1978.
20. CLIMIP10 2',2'',2''-TRICHLOROETHYL-2-(2-BENZYL-4-METHOXY-CARBONYL-1-IMIDAZOLYL)-3-METHYL-ISOCROTONATE B.KOJIC-PROJIC,Z.RUZIC-TOROS, ACTA CR., B36,2726,1980.
21. CLMPM0 5-CHLORO-6-DICHLOROMETHYLENE-4-METHOXY-1-METHYL-4-TRICHLOROMETHYL-HEXAHYDROPYRIMIDIN-2-ONE C.H.STAM, ACTA CR., B36,729,1980.
22. CNMFLU10 9-DICYANOMETHYLENE-2,4,5,7-TETRANITROFLUORENE J.SILVERMAN ET AL, ACTA CR., B30,1474,1974.
23. CUAQAC21 TETRA-MU-ACETATO-BIS(AQUO)-DICOPPER(II) (N) G.M.BROWN,R.CHIDAMBARAM, ACTA CR., B29,2393,1973.
24. CYSTCL02 L-CYSTEINE DIHYDROCHLORIDE (N) D.D.JONES ET AL, ACTA CR., B30,1220,1974.
25. DETBA04 5,5-DIETHYLBARBITURIC ACID (FORM II, 198 K) (N) R.K.MCMULLAN ET AL, ACTA CR., B34,3719,1978.
26. DETSBR01 1,3-DIETHYL-2-THIOBARBITURIC ACID (N) J.-P.BIDEAU,G.BRAVIC,A.FILHOL, ACTA CR., B33,3847,1977.
27. DMAH0X01 DIMETHYLAMMONIUM HYDROGEN OXALATE (N) J.O.THOMAS, ACTA CR., B33,2867,1977.
28. DNITPY 3,5-DINITROPYRIDINE R.DESTRO,T.PILATI,M.SIMONETTA, ACTA CR., B30,2071,1974.
29. DNPHL 2,6-DINITROPHENOL T.KAGAWA ET AL, ACTA CR., B32,3171,1976.
30. DNBUPA01 3I-T-BUTYLPHOSPHINE ACID (N) A.H.REIS JR ET AL, INORG.CHEM., 15, 2749,1976.
31. DURENE01 DURENE (N) E.PRINCE,L.W.SCHROEDER,J.J.RUSH, ACTA CR., B29,184,1973.
32. FACTNS TRIFLUOROACETYL-TRISULFUR-TRINITRIDE R.STEUDER ET AL, Z.NATURFORSCH.,TEIL B, 32,488,1977.
33. FMANIL N-METHYL-2,6-DINITRO-4-TRIFLUOROMETHYL-ANILINE J.N.BROWN,R.L.R.TOWNS, ACTA CR., B33,149,1977.
34. FMBOPS 2,2,3,3-TETRAKIS (TRIFLUOROMETHYL)-5-T-BUTYL-7,8-BENZO-1,4,6,9-TETRAOXA-5-PHOSPHASPIRO(4,4)NONENE R.K.BROWN,R.O.DAVY,S.HUSEBYE,R.R.HOLMES, INORG.CHEM., 17,3276,1978.
35. FMPZTZ10 1-(4-METHYL-1-PYRAZOLIN-3-YL)-5,5-BIS (TRIFLUOROMETHYL)-CDELTA-2--1,2,3-TRIAZOLINE A.GIEREN, CHEM.BER., 106,288,1973.
36. FMSTLB (E)-ALPHA-TRIFLUOROMETHYL-STILBENE G.RUBAN ET AL, CHEM.BER., 113,3384,1980.
37. GLICHC01 GLYCYLYLGLYCINE HYDROCHLORIDE MONOHYDRATE (N) T.F.KOETZLE ET AL, ACTA CR., B28,2083,1972.
38. GUMOAS02 GUANIDINIUM (MU-4-HYDROXY)-BIS (MU-3-OXO)-TETRAKIS (MU-2-OXO)-TETRAKIS (DIOXO-MOLYBDENUM)-DIMETHYLARSINATE MONOHYDRATE K.M.BARKICIA,L.M.RAJKOVIC-BLAZER,M.T.POPE,E.PRINCE,C.O.QUICKSALL, INORG.CHEM., 19,2511,1980.
39. HMPFPE 2-HYDROXY-1,1,2,2-TETRAKIS (TRIFLUOROMETHYL)-ETHYL-DIMETHYLPHOSPHINATE D.SCHOMBURG,O.STELZER,N.WEFLERLING,R.SCHMUTZLER,W.S.SHELDRIK, CHEM.BER., 113,1566,1980.
40. HMPIC01 MU-3-HYDRIDO-MU-3-(TRICARBONYL-IRON)-TRIANGULO-(TRI-MU-CARBONYL-TRIS(CARBONYL-TRIMETHYLPHOSPHITE-COBALT)) (90 K) (N) R.G.TELLER,R.D.WILSON,R.K.MCMULLAN,T.F.KOETZLE,R.BAU, J.AM.CHEM.SOC., 100,3071,1978.
41. KCLEPT03 POTASSIUM TRICHLOROETHYLENE PLATINATE MONOHYDRATE (ZEISE'S SALT) (N) R.A.LOVE,T.F.KOETZLE,G.J.B.WILLIAMS,L.C.ANDREWS,R.BAU, INORG.CHEM., 14,2653,1975.
42. LALNIN12 L-ALANINE (N) M.S.LEHMANN,T.F.KOETZLE,W.C.HAMILTON, J.AM.CHEM.SOC., 94,2657,1972.
43. LIHPM01 METHANOL SOLVATE IN LITHIUM HYDROGEN PHTHALATE (N) H.KUPPERS ET AL, ACTA CR., B37,1203,1981.
44. MALTPY01 METHYL ALPHA-D-ALTOPYRANOSIDE (N) B.J.POPPLETON ET AL, ACTA CR., B31,2400,1975.
45. MATQI69 TRIMETHYLAMMONIUM 7,7,8,8-TETRACANOQUINOIMIDOMETHANE TRI-IODIDE (80 K) (N) A.FITZEL,J.GAULTIER, ACTA CR., B36,592,1980.
46. MCFAP2P 1,3-DIMETHYL-2,4-BIS (TRICHLOROMETHYL)-2,2,4,4-TETRAFLUORO-1,3-DIAZA-2,4-DIPHOSPHETIDINE W.S.SHELDRIK,M.J.C.HEWSON, ACTA CR., B31,1209,1975.
47. MEADEN02 9-METHYLADENINE (126 K) (N) R.K.MCMULLAN,P.BENCI,B.M.CRAVEN, ACTA CR., B36,1424,1980.
48. MELAM104 2,4,6-TRIAMINO-1,3,5-TRIAZINE (MELAMINE) (N) J.N.VARGHESE ET AL, ACTA CR., B33,2102,1977.
49. MEMANP11 METHYL-D-MANNOPIRANOSIDE (N) G.A.JEFFREY ET AL, ACTA CR., B33,728,1977.
50. METHYM01 1-METHYLTHYMINE (N) A.KVICK,T.F.KOETZLE,R.THOMAS, J.CHEM.PHYS., 61,2711,1974.
51. MGLUCP11 METHYL ALPHA-D-GLUCOPYRANOSIDE (N) G.A.JEFFREY ET AL, ACTA CR., B33,728,1977.
52. MNHCA 2,3,4,5-DIMETHANO-2,4-DINITRO-1-HYDROXYCYCLOHEXANE-1-CARBOXYLIC ACID J.BEINTEMA, ACTA CR., B32,1631,1976.
53. MYTHAD11 9-METHYLADENINE - 1-METHYLTHYMINE COMPLEX (N) M.FREY ET AL, J.CHEM.PHYS., 59,915,1973.
54. NAHACE01 SODIUM HYDROGEN DIACETATE (N) M.J.BARRON ET AL, J.CHEM.SOC.,PERKIN 2, 15,1975.
55. NANIL1 4-NITROANILINE K.N.TRUEBLOOD,E.GOLDSB,J.DONOHUE, ACTA CR., 14,1089,1961.
56. NEBSMS N-(1-ALPHA-NAPHTHYLETHYL)-N-(BENZENESULFONYL)TRICHLOROETHANESULFENAMIDE J.KAY ET AL, J.AM.CHEM.SOC., 93,5224,1971.
57. NMZNON 1,5-DINITRO-3-METHYL-3-AZABICYCLO(3.3.1)NONAN-7-ONE (FORM A) M.KAFTORY,J.D.DUNITZ, ACTA CR., B32,1,1976.
58. NMZNON01 1,5-DINITRO-3-METHYL-3-AZABICYCLO(3.3.1)NONAN-7-ONE (FORM B) M.KAFTORY,J.D.DUNITZ, ACTA CR., B32,1,1976.
59. NPCBNZ 3-NITROPERCHLORYL BENZENE G.J.PALENIK,J.DONOHUE,K.N.TRUEBLOOD, ACTA CR., B24,1139,1968.
60. NPYTAQ10 BIS (MU-2-CHLORO)-BIS (DICHLORO-NEOPENTYLIDENE-TRIMETHYLPHOSPHINE-TANTALUM) (110 K) (N) A.J.SCHULTZ,R.K.BROWN,J.M.WILLIAMS,R.R.SCHROCK, J.AM.CHEM.SOC., 103,169,1981.
61. OCLOCT MESO-(RS)-1,1,3,3,6,8,8,8-OCTACHLORO-OCTANE J.C.J.BART ET AL, ACTA CR., B35,2646,1979.
62. OPHDAH01 1,2-DIAMINO BENZENE MONOHYDROCHLORIDE (N) C.STALHANDSKE, ACTA CR., B32,2806,1976.
63. PCPYXL PERCHLORO-P-XYLENE X.SOLANS,S.GALI,C.MARAVITTES,M.EOY-ALTAHA, ACTA CR., B34,3790,1978.
64. PHALNC01 L-PHENYLALANINE HYDROCHLORIDE (N) A.R.AL-KARAGHOULI,T.F.KOETZLE, ACTA CR., B31,2461,1975.
65. PRCHLA 2,4,6-TRIS (TRICHLOROMETHYL)-1,3,5-TRIOXANE D.G.HAY,M.F.MACKAY, ACTA CR., B36,2367,1980.
66. PXRBA10 T-BUTYLAMMONIUM 3,6,9,12,15-PENTAOXABICYCLO(15.3.1)HENEICOSA-1(12),17,19-TRIENE-21-CARBOXYLATE (120 K) I.GOLDBERG, ACTA CR., B31,2592,1975.
67. PYCRBA10 MONOPYRIDO-18-CROWN-6 T-BUTYLAMMONIUM PERCHLORATE COMPLEX (113 K) E.MAVERICK ET AL, ACTA CR., B35,2233,1979.
68. PYRXCL01 PYRIDOXINIUM CHLORIDE (N) G.E.BACON,J.S.PLANT, ACTA CR., B36,1130,1980.
69. TACBEN01 1,3,5-TRIACETYL BENZENE (N) B.H.O'CONNOR,F.H.MOORE, ACTA CR., B29,1903,1973.
70. TUBEN10 1,2,4,5-TETRA-T-BUTYLBENZENE C.H.STAM, ACTA CR., B28,2715,1972.
71. TUNAP 1,3,6,8-TETRA-T-BUTYLNAPHTHALENE J.HANDAL ET AL, J.AM.CHEM.SOC., 99,3345,1977.
72. TZBZBA N-METHYL-N-BENZYL-2,4,6-TRI-T-BUTYLBENZAMIDE A.E.JUNGK,G.M.J.SCHMIDT, CHEM.BER., 104,3289,1971.
73. TBUUD0 TRANS-3,4-DI-T-BUTYLCYCLOBUTANEDIONE J.K.COLEMAN ET AL, ACTA CR., B32,115,1976.
74. TNAHOX TRIMETHYLAMMONIUM HYDROGEN OXALATE J.O.THOMAS,N.RENNE, ACTA CR., B31,2161,1975.
75. TMTB10 1,2-DI-T-BUTYL-3,4,5,6-TETRAMETHYLBENZOCYCLOBUTADIENE W.WINTER,T.BUTTERS, ACTA CR., B37,1524,1981.
76. TNAPHA (R)-N-TRIFLUOROACETYL-1-(1-NAPHTHYL)-ETHYLAMINE S.WEINSTEIN,L.LEISEROWITZ, ACTA CR., B36,1406,1980.
77. TOLSA01 DEUTERIUM P-TOLUENESULFONATE (N) J.E.FINHOLT,J.M.WILLIAMS, J.CHEM.PHYS., 59,514,1973.
78. TOLSAM12 P-TOLUENESULFONIC ACID MONOHYDRATE (N) J.-O.LUNDGREN,J.M.WILLIAMS, J.CHEM.PHYS., 58,788,1973.
79. VALEHC11 L-VALINE HYDROCHLORIDE (N) T.F.KOETZLE ET AL, J.CHEM.PHYS., 60,4690,1974.
80. \* \* \* ACETAMIDE HEMIHYDROCHLORIDE (120 K) (N) J.C.SPEAKMAN ET AL, ACTA CR., B37,2090,1981.
81. N-ACETYL-L-CYSTEINE (16K) (N) F.TAKUSAGAWA ET AL, ACTA CR., B37,1591,1981.
82. BRIDGED SPHERAND, C50,H48,06.LI+.FECL4- (113 K) D.J.CRAM ET AL, J.AM.CHEM.SOC., 103,6228,1981.
83. BRIDGED SPHERAND, C50,H48,06.LI+.CL- (113K) D.J.CRAM ET AL, J.AM.CHEM.SOC., 103,6228,1981.
84. T-BUTYLAMMONIUM CHLORIDE (113 K) K.N.TRUEBLOOD, UNPUBLISHED
85. T-BUTYLAMMONIUM CHLORIDE (296 K) K.N.TRUEBLOOD, UNPUBLISHED
86. 2,6-DI-(2-ANISYL)-CYCLOHEXANONE K.N.TRUEBLOOD, UNPUBLISHED
87. 3,7-DI-T-BUTYL-5-PHENYL-2-P-TOLYL-OXEPIN A.RIEKER ET AL, CHEM.BER., 115,385,1982.
88. NN'-DI-(T-BUTYL)-SULFAMIDE J.L.ATWOOD ET AL, INORG.CHEM., 21,435,1982.
89. 1,1'-DINITRO-BICYCLOBUTYL (173 K) Y.KAI ET AL, HELV.CHIM.ACTA, 65,137,1982.
90. 1,1'-DINITRO-BICYCLOPROPYL (95 K) Y.KAI ET AL, HELV.CHIM.ACTA, 65,137,1982.
91. 2,3-DIMETHYL-2,3-DINITROBUTANE (95 K) Y.KAI ET AL, HELV.CHIM.ACTA, 65,137,1982.
92. FORMAMIDE OXIME (16 K) (N) G.A.JEFFREY ET AL, ACTA CR., B37,1381,1981.
93. MONOFLUOROACETAMIDE (20 K) (N) G.A.JEFFREY ET AL, ACTA CR., B37,1381,1981.
94. SPHERAND, C48,H48,06 K.N.TRUEBLOOD ET AL, J.AM.CHEM.SOC., 103,5994,1981.
95. SPHERAND, C48,H48,06.LI+.CL- K.N.TRUEBLOOD ET AL, J.AM.CHEM.SOC., 103,5994,1981.
96. SPHERAND, C48,H48,06.NA+.CH3SO4- K.N.TRUEBLOOD ET AL, J.AM.CHEM.SOC., 103,5994,1981.
97. SPHERAND, C64,H48,08 K.N.TRUEBLOOD, UNPUBLISHED.

intramolecular part of the force field should be relatively independent of temperature whereas the intermolecular part should vary with change in unit-cell dimensions and intermolecular distances, careful studies of the temperature dependence of torsional force constants and barriers of particular groups in crystals could be very rewarding.

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## APPENDIX

### Bibliography of structures (Table 2)

Structures are referred to by number in the text, figures and Table 1. Those included in the Cambridge Database files through May 1982 are arranged alphabetically in the order of their REFCODES (Allen *et al.*, 1979); others are grouped together at the end, in alphabetical order of compound names. Some references have been abbreviated to save space.

(N) indicates a neutron diffraction structure analysis. For structures determined at other than room temperature, the temperature is given.

The letters *A* and *B* after structure numbers in Figs. 3 and 5 designate the same group in crystallographically independent molecules in a given structure.

### References

- AFONINA, N. N. & ZORKII, P. M. (1976). *J. Struct. Chem.* **17**, 13–15.
- ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* **B35**, 2331–2339.
- ALLEN, G. & FEWSTER, S. (1974). In *Internal Rotation in Molecules*, edited by W. J. ORVILLE-THOMAS. London, New York: Wiley-Interscience.
- BAAS, J. M. A., VAN DE GRAAF, B., VAN VEEN, A. & WEPSTER, B. M. (1980). *Recl Trav. Chim. Pays Bas*, **99**, 228–233.
- BROCK, C. P. & DUNITZ, J. D. (1982). *Acta Cryst.* **B38**, 2218–2228.
- BROWN, K. L., DAMM, L., DUNITZ, J. D., ESCHENMOSER, A., HOBI, R. & KRATKY, C. (1978). *Helv. Chim. Acta*, **61**, 3108–3135.
- BÜRGER, H., NIEPEL, H. & PAWELKE, G. (1980). *Spectrochim. Acta Part A*, **36**, 7–15.
- BÜRGI, H. B. & SHEFTER, E. (1975). *Tetrahedron*, **31**, 2976–2981.
- CAMINATI, W. (1982). *J. Chem. Soc. Faraday Trans. 2*, **78**, 825–838.
- CHAKRABARTI, P., SEILER, P., DUNITZ, J. D., SCHLÜTER, A.-D. & SZEIMIES, G. (1981). *J. Am. Chem. Soc.* **103**, 7378–7380.
- CORRELL, T., LARSEN, N. W. & PEDERSEN, T. (1980). *J. Mol. Struct.* **65**, 43–49.
- CRAM, D. J. & TRUEBLOOD, K. N. (1981). *Top. Curr. Chem.* **98**, 43–106.
- CRUICKSHANK, D. W. J. (1956a). *Acta Cryst.* **9**, 754–756.
- CRUICKSHANK, D. W. J. (1956b). *Acta Cryst.* **9**, 1005–1009.
- CRUICKSHANK, D. W. J. (1956c). *Acta Cryst.* **9**, 1010–1011.
- CYVIN, S. J., CYVIN, B. N., HAGEN, G., CRUICKSHANK, D. W. J. & PAWLEY, G. S. (1972). *Molecular Structures and Vibrations*, edited by S. J. CYVIN, pp. 299–309. Amsterdam: Elsevier.
- DUNITZ, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, pp. 244–261. Cornell Univ. Press.
- DUNITZ, J. D. & WHITE, D. N. J. (1973). *Acta Cryst.* **A29**, 93–94.
- DURIG, J. R. & BROWN, S. C. (1976). *J. Mol. Struct.* **31**, 11–21.
- DURIG, J. R. & CHURCH, J. S. (1980). *Spectrochim. Acta Part A*, **36**, 957–964.
- DURIG, J. R., CRAVEN, S. M., MULLIGAN, J. H., HAWLEY, C. W. & BRAGIN, J. (1973). *J. Chem. Phys.* **58**, 1281–1291.
- DURIG, J. R., PLAYER, C. M. JR, BRAGIN, J. & LI, Y. S. (1971). *J. Chem. Phys.* **55**, 2895–2905.
- FATELEY, W. G., HARRIS, R. K., MILLER, F. A. & WITKOWSKI, R. E. (1965). *Spectrochim. Acta*, **21**, 231–244.
- GAVEZZOTTI, A. & SIMONETTA, M. (1982). *Chem. Rev.* **82**, 1–13.
- HAMILTON, W. C., EDMONDS, J. W., TIPPE, A. & RUSH, J. J. (1969). *Discuss. Faraday Soc.* **48**, 192–204.
- HIRSHFELD, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- HIRSHFELD, F. L. & SHMUELI, U. (1972). *Acta Cryst.* **A28**, 648–651.
- HØG, J. H., NYGAARD, L. & SØRENSEN, G. O. (1971). *J. Mol. Struct.* **7**, 111–121.
- JEFFREY, G. A., RUBLE, J. R., McMULLAN, R. K., DEFREES, D. J., BINKLEY, J. S. & POPLE, J. A. (1980). *Acta Cryst.* **B36**, 2292–2299.
- JOHNSON, C. K. (1969). *Acta Cryst.* **A25**, 187–194.
- JOHNSON, C. K. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS, ch. 9, pp. 132–160. Oxford Univ. Press.
- JONES, D. D., BERNAL, I., FREY, M. N. & KOETZLE, T. F. (1974). *Acta Cryst.* **B30**, 1220–1227.
- KAI, Y., KNOCHEL, P., KWATKOWSKI, S., DUNITZ, J. D., OTH, J. F. M. & SEEBACH, D. (1982). *Helv. Chim. Acta*, **65**, 137–161.
- KALASINSKY, V. F. & ANJARIA, H. V. (1980). *J. Phys. Chem.* **84**, 1940–1944.
- KANESAKA, I., NAKA, H. & KAWAI, K. (1979). *J. Chem. Phys.* **70**, 5773–5777.
- KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*, pp. 18–21. London, New York: Academic Press.
- LAMBERT, J. B., NIENHUIS, R. J. & FINZEL, R. B. (1981). *J. Phys. Chem.* **85**, 1170–1172.
- LEHMANN, M. S., KOETZLE, T. F. & HAMILTON, W. C. (1972). *J. Am. Chem. Soc.* **94**, 2657–2660.
- LISTER, D. G., MACDONALD, J. N. & OWEN, N. L. (1978). *Internal Rotation and Inversion. An Introduction to Large Amplitude Motions in Molecules*. London, New York: Academic Press.
- LOWE, J. P. (1968). *Progress in Physical Organic Chemistry*. Vol. 6, edited by A. STREITWEISER JR & R. W. TAFT, pp. 1–80. New York: Wiley-Interscience.
- MEYER, R., GAMMETER, A., SMITH, P., KÜHNE, H., NÖSBERGER, P. & GÜNTARD, Hs. (1973). *J. Mol. Spectrosc.* **46**, 397–400.
- MOCHEL, A. R., BRITT, C. O. & BOGGS, J. E. (1973). *J. Chem. Phys.* **58**, 3221–3229.
- ORVILLE-THOMAS, W. J. (1974). Editor. *Internal Rotation in Molecules*. London, New York: Wiley-Interscience.
- OWEN, N. L. & HESTER, R. E. (1969). *Spectrochim. Acta*, **25**, 343–354.
- PRINCE, E., DICKENS, B. & RUSH, J. J. (1974). *Acta Cryst.* **B30**, 1167–1172.
- PRINCE, E., SCHROEDER, L. W. & RUSH, J. J. (1973). *Acta Cryst.* **B29**, 184–191.
- RALOWSKI, W. & LJUNGGREN, S. (1977). *Acta Chem. Scand. Part A*, **31**, 492–494.
- RATCLIFFE, C. J. & DUNELL, B. A. (1978). *Faraday Symp. Chem. Soc.* **13**, 142–152.

- RIAND, J., CHENON, M.-T. & LUMBROSO-BADER, N. (1980). *Can. J. Chem.* **58**, 466–471.
- ROSENFELD, R. E., TRUEBLOOD, K. N. & DUNITZ, J. D. (1978). *Acta Cryst.* **A34**, 828–829.
- RUSH, J. J. (1967). *J. Chem. Phys.* **47**, 3936–3943.
- SCHLEMPER, E. O., HAMILTON, W. C. & LAPLACA, S. J. (1971). *J. Chem. Phys.* **54**, 3990–4000.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SCHWEIZER, W. B., PROCTER, G., KAFTORY, M. & DUNITZ, J. D. (1978). *Helv. Chim. Acta*, **61**, 2783–2808.
- SEILER, P. & DUNITZ, J. D. (1979). *Acta Cryst.* **B35**, 2020–2032.
- SEILER, P. & DUNITZ, J. D. (1980). *Acta Cryst.* **B36**, 2946–2950.
- SPEAKMAN, J. C. (1975). *Mol. Struct. Diffr. Methods*, **3**, 93.
- SUNNERS, B., PIETTE, L. H. & SCHNEIDER, W. G. (1960). *Can. J. Chem.* **38**, 681–688.
- THOMAS, L. P., TRUE, N. S. & BOHN, R. K. (1980). *J. Phys. Chem.* **84**, 1785–1789.
- TRUEBLOOD, K. N. (1978). *Acta Cryst.* **A34**, 950–954.
- TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009–1017.
- TRUEBLOOD, K. N., KNOBLER, C. B., LAWRENCE, D. S. & STEVENS, R. V. (1982). *J. Am. Chem. Soc.* **104**, 1355–1362.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
- YODER, C. H. & GARDNER, R. D. (1981). *J. Org. Chem.* **46**, 64–66.

*Acta Cryst.* (1983). **B39**, 133–138

## Comparison of X-ray and Neutron Diffraction Results for the N—H···O=C Hydrogen Bond

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### Abstract

The errors associated with X-ray determinations of N—H···O=C hydrogen-bond geometries have been analysed. The analysis was based on a comparison of X-ray and neutron diffraction results for 57 hydrogen bonds which have been determined by both methods. The random errors in X-ray N—H and H···O distances were found to vary between 0.02–0.17 Å, the mean value being 0.065 Å. These errors exceed the e.s.d.'s quoted in the literature by a factor of approximately 1.6. The average systematic error in the X-ray N—H and H···O distances is about 0.1 Å. However, systematic errors can be corrected by 'normalizing' the N—H bond lengths to a standard value (1.030 Å).

### Introduction

The N—H···O=C hydrogen bond plays a major role in determining the conformations of proteins and nucleic acids (Pimentel & McClellan, 1960). Consequently, its geometry has been investigated extensively by crystallographic techniques. Early X-ray diffraction studies of amino acids and nucleosides provided detailed information about the distribution of N···O distances (Ramakrishnan & Prasad, 1971). However, the values of the true hydrogen-bond lengths (*i.e.* H···O) and N—H···O angles were obscured by the large experimental uncertainties in the hydrogen-

atom positions. Unfortunately, the N···O distance is an unreliable guide to the strength of a hydrogen bond; *e.g.* the six N—H···O bonds in Table 1 (determined by neutron diffraction) have almost identical N···O distances but H···O distances ranging from 1.844 (2) to 2.083 (6) Å.

Recent reviews of N—H···O hydrogen-bond geometries have therefore relied extensively on the results of neutron diffraction studies, which provide precise information about the H···O distances and N—H···O angles (*e.g.* Jeffrey & Maluszynska, 1982; Koetzle & Lehmann, 1976; Olovsson & Jönsson, 1976; see also Ceccarelli, Jeffrey & Taylor, 1981; Taylor & Kennard, 1982, for studies of other types of hydrogen bonds using neutron data). However, neutron studies con-

Table 1. Selected hydrogen-bond geometries determined by neutron diffraction

Structure	Hydrogen bond <sup>a</sup>	N···O (Å)	H···O (Å)	Reference number in Table 2
L-Lysine mono-hydrochloride dihydrate	N(2)—H(4)···O(2)	2.887 (3)	2.083 (6)	22
Hydrazinium hydrogen oxalate	N(2)—H(2)···O(1)	2.884 (1)	1.935 (2)	12
9-Methyladenine-1-methylthymine	N(10')—H(4)···O(8)	2.872 (3)	1.932 (5)	23
L-Glutamic acid	N(1)—H(2)···O(11)	2.895 (1)	1.926 (2)	18
L-Tyrosine	N(1)—H(3)···O(2)	2.884 (2)	1.853 (4)	21
DL-Serine	N(1)—H(2)···O(2)	2.876 (1)	1.844 (2)	6

(<sup>a</sup>) Atom labels are those used in the Cambridge Structural Database.